Switchable Mirrors.

Griessen, R.P.

published in
Europhysics News
2001

DOI (link to publisher)
10.1051/epn:2001201

document version
Publisher's PDF, also known as Version of record

Switchable Mirrors

R. Griessen
Faculty of Sciences, Division of Physics and Astronomy, Vrije Universiteit, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands

The discovery

In 1990, in the middle of the euphoric times of high-temperature superconductivity, we decided to search for other superconductors with a potentially high T_c. Since there were predictions that solid, metallic atomic hydrogen might become superconducting at temperatures as high as 200-250 K, we looked into the possibility to create new superconductors based on hydrogen. However, instead of trying to metallize pure hydrogen under very high pressures, we chose another route. We first incorporated hydrogen into a metal to break the molecular bond of H_2 and started to compress the sample under high pressures (not higher than 0.5 GPa) to increase its metallic character, thus favoring superconductivity.

As starting material we chose yttrium, which is able to absorb 300% hydrogen up to the composition YH_3. We evaporated a 500 nm thick yttrium film on one of the diamonds of a high pressure diamond-anvil-cell. Quite unexpectedly, upon hydrogen uptake under several thousands of atmospheres, around 240 K, the yttrium film changed from a shiny metallic into a transparent yellowish sample [1]. Although metal-insulator transitions had already been described in earlier work on rare-earth hydrides [2], no report whatsoever existed about such drastic changes in their visible optical properties, most probably because nobody really looked at hydrides during hydrogen uptake. Our great fortune was that the diamond-anvil-cell allowed us to optically monitor the hydrogen absorption *in situ*!

Very much intrigued by these spectacular changes, we tried to induce the same transition at room temperature and low hydrogen gas pressure (typically 1 bar). It worked admirably, provided the yttrium film was protected by a thin layer (5-20 nm) of palladium. With this protective layer we could take samples out of the ultra-high vacuum deposition system without danger of oxidation (a severe problem with highly reactive materials such as yttrium and rare-earths) and carry out a whole series of *ex situ* experiments (temperature dependence of the resistivity, magnetoresistance, Hall effect, photoconductivity, pressure dependence of the semiconducting gap, optical transmission and reflection, etc.) which are usually impossible on the corresponding *bulk* materials as hydrogenation reduces their trihydrides into powder.

Optical switching

The simplest way to get an impression of what switchable mirrors really are is to follow the changes which occur in an yttrium film during loading with hydrogen at room temperature. Figure 1 exhibits the evolution of the electrical resistivity and optical transmission for red light (with $\hbar\omega = 1.96$ eV) as a function of the time elapsed since the film has been brought into contact with hydrogen gas at 10^5 Pa. As the hydrogen uptake occurs approximately linearly, the time axis is essentially also a hydrogen concentration axis. Spectacular changes occur in both the electrical and optical properties. After a weak rise due to impurity scattering the electrical resistivity ρ decreases steadily until it reaches a minimum in the dihydride phase. YH_2 has at this point an electrical resistivity which is about 5 times *lower* than that of pure Y. At higher concentrations ρ increases by several orders of magnitude and is only limited by the conductivity of the 20 nm Pd caplayer. The optical transmittance remains low until in the dihydride phase a weak maximum occurs at approximately the same time as the minimum in ρ is reached. As demonstrated by Den Broeder *et al.* [3], this weak red transparency is most valuable for the visualization of hydrogen diffusion as it makes it possible to locate exactly the YH_2 phase in a diffusion experiment. The film transmittance suddenly rises and stays high as the H concentration is increased from 2 to 3. These changes are easily observed as a switch from high to low reflectivity and significant transmittance in the last two photographs of Fig.1. The transition back from the transparent trihydride to the shiny dihydride is reversibly induced by decreasing the surrounding hydrogen gas pressure. Gas loading is easily carried out; for a direct measurement of the hydrogen concentration it is necessary to use instead electrolytic charging. The time-integrated electrical current flowing in an oxygen-free electrolytic cell during hydro-

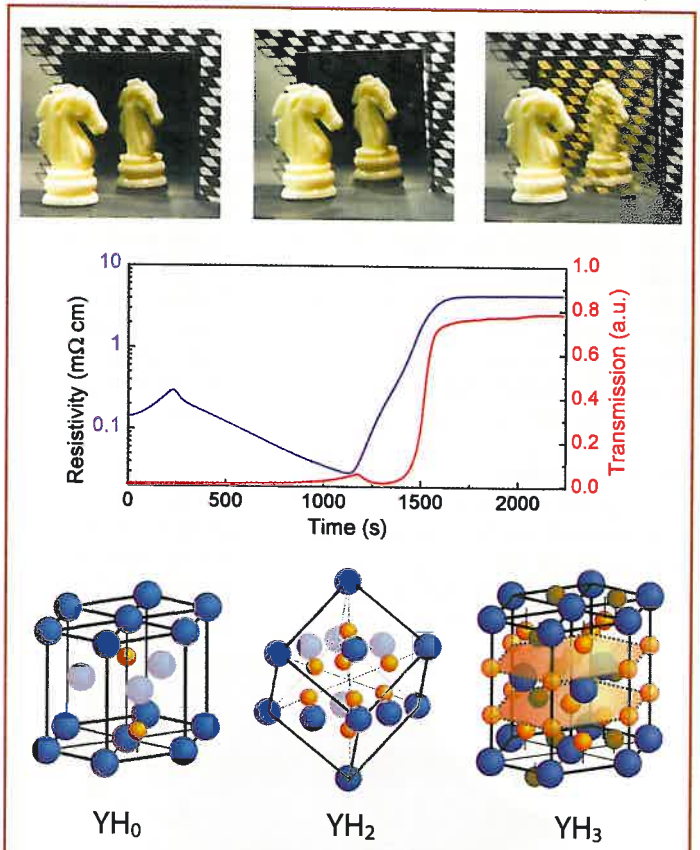


Fig. 1: Variation of the electrical resistivity and optical transmittance $\hbar\omega = 1.96$ eV) of a 300 nm thick yttrium film protected by a 20 nm thick Pd caplayer brought in contact with H_2 gas at 10^5 Pa pressure at room temperature. The hydrogen concentration is approximately proportional to the elapsed time *t*, except after 1600 s where both electrical resistivity and optical transmittance have reached saturation. This experiment is deliberately carried out slowly, but optical switching can in fact be much faster (see Fig. 4). The photographs illustrate the reflectance and transmittance of the film as deposited, in the dihydride and in the trihydride phase. The structures of the various phases are schematically depicted in the lower panel.

Article available at http://www.europhysicsnews.org or http://dx.doi.org/10.1051/epn:2001201

gen charging is a direct measure of the number of H injected into the switchable mirror. Measurements of optical transmittance and reflectance and other parameters as a function of H concentration are then possible. Whereas the drop in transmittance above $\hbar\omega = 2.8$ eV in YH_3 in Fig.2 is due to the onset of optical absorption, the oscillations in reflectance are due to multiple reflections within the sample.

Metal-insulator transition

The increase in ρ with increasing H concentration in Fig.1 and the decrease of the reflectance in Fig. 2 are indications of the occurrence of a metal-insulator (MI) transition. At first sight this MI-transition seems to have a rather trivial origin. As seen in Fig.1, YH_2 has a cubic structure while YH_3 is hexagonal. Many such transitions in nature are of first order (for example diamond to graphite, white to grey tin, vanadium oxides). In fact, YH_x is already in the hexagonal phase when the MI-transition occurs around x=2.86. YH_x is, therefore, one of the very few examples of a system with a *continuous* MI-transition; this alone makes it a fascinating material. In addition, the ease at which the H concentration can be modified is a tremendous advantage for experimental investigations. Instead of having to painstakingly prepare a whole series of samples with various degrees of doping (for example boron doped silicon, or Se substituted NiS_2) one can simply actuate a switchable mirror by controlling the surrounding hydrogen gas pressure or the voltage in an electrolytic cell.

The MI-transition is also *robust* in the sense that it occurs in all hydrides of the trivalent rare-earths. They all switch optically when the H concentration is increased from 2 to 3 although the crystal structure of the trihydrides can be hexagonal as for YH_3, cubic as for LaH_3 or more complicated as for SmH_3. A MI-transition also occurs in *cubic* YH_3 and in disordered alloys of yttrium and lanthanum, whose trihydrides are either cubic or hexagonal, depending on the composition [4]. In the trihydride state they are all transparent albeit with characteristic colors: for example, YH_3 is yellowish, LaH_3 red, while some alloys are colorless.

Theoretical models

Although the occurrence of a MI-transition in YH_x could have been expected on the basis of earlier work on bulk rare-earth hydrides [2], the transparency of $YH_{3-\delta}$ discovered by Huiberts *et al.* [1] came as a great surprise, since the state-of-the-art self-consistent band structure calculations in the early nineties predicted YH_3 to be a semi-metal with, in fact, a considerable band *overlap* (1.5 eV). The occurrence of large optical gaps in YH_3 and LaH_3, as well as the observed increase in resistivity with decreasing temperature, being incompatible with a metallic character, stimulated theorists to reconsider the YH_x and LaH_x systems in detail.

Somewhat as for the high-T_c superconductors two lines of thought developed:

i) **Band structure models:** Originally it was proposed that the semiconducting ground state of YH_3 was due to a so-called Peierls distortion of the crystal lattice. The total energy of YH_3 was indeed found to be extremely sensitive to the exact position of the H atoms, especially those close to the Y planes. So far, however, no experimental evidence has been found for the existence of a low symmetry crystal structure of YH_3. Very recently van Gelderen *et al.* [5] demonstrated that improved band structure calculations based on the so-called GW approximation led to a fundamental direct but dipole forbidden energy gap of 1 eV and an indirect optical gap of almost 3 eV without having to invoke any lattice distortion. The agreement of these calculations with the optical data is remarkable since they do not involve any fit parameters. A similar approach predicted that also *cubic* YH_3 should be a semiconductor.

ii) **Strong electron correlation models:** Other theorists [6] expected strong correlation effects to be especially large in YH_x and similar rare-earth-hydrides as a direct consequence of the large on-site repulsion between two electrons near the same proton. This repulsion is reflected in the radius of the negative H^--ion that is about 3 times larger than for a neutral H atom and its ionization potential, which is only 0.7 eV compared to 13.6 eV for neutral H. Electron correlation leads to a drastic narrowing of the H-derived band and therefore to a sizeable gap between this low-lying band and the La-derived 5d-bands in LaH_x or the Y-derived 4d-bands in YH_x. The swelling of neutral H when it transforms to an H^--ion led to the new concept of a *breathing* Hubbard Hamiltonian.

The GW calculations provide no direct insight into the mechanism of the metal-insulator transition. The strong electron correlation picture, however, leads to the following scenario first proposed by Sawatzky and co-workers. For simplicity, we consider the case of LaH_x. Although metallic La is hexagonal, LaH_2 is cubic with all tetrahedral sites occupied by H atoms (CaF_2 structure).

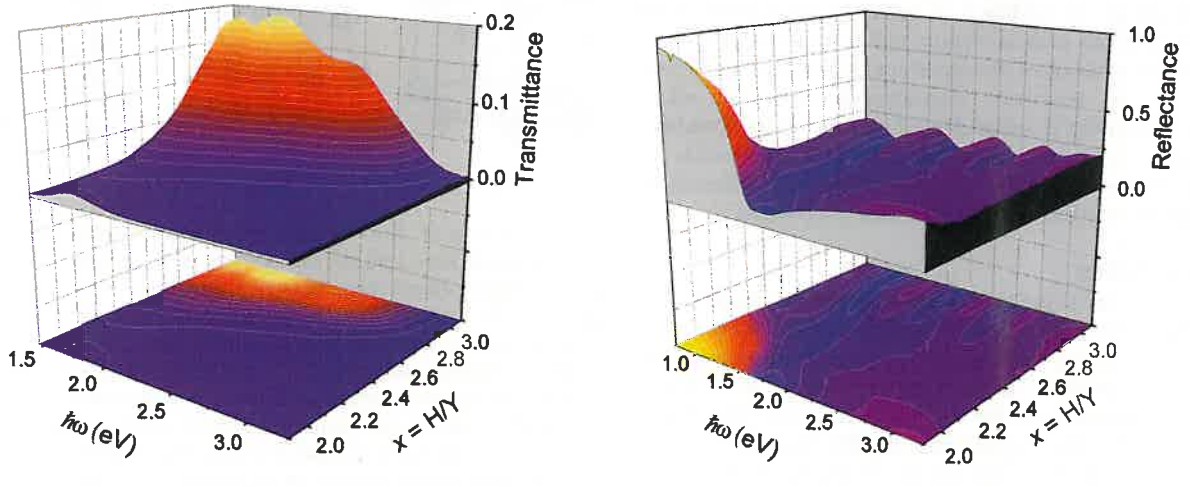


Fig. 2: Hydrogen concentration and photon energy dependence of a) the optical transmittance and b) the reflectance of a 300 nm thick yttrium film protected by a 15 nm thick Pd caplayer.

These H atoms are so strongly bound that they are not involved in the MI-transition that occurs around $LaH_{2.8}$. The nice thing about LaH_x at room temperature, is that it remains cubic all the way up to LaH_3. Each H added to LaH_2 occupies octahedral sites with six La nearest neighbors. It attracts a conduction electron to form a singlet in a way similar to what happens with two holes in high-T_c superconducting cuprates. One electron is on an orbital localized around the proton (with a radius of ≃ 0.5 Å) and the other is race-tracking on the neighboring La atoms (see Fig.3). Roughly speaking this resembles a huge H^--ion with a diameter of the order of the host lattice spacing (≃ 6 Å). As every H ties up an electron from the conduction band, electrical conductivity becomes increasingly difficult and the system tends towards a so-called Kondo-insulator. In an alternative picture, one may start from insulating LaH_3 and create vacancies in the octahedral H sublattice. Ng *et al.* [6] argue that H-vacancies are highly localized donors. This explains why 0.2 vacancies per La (a huge doping level compared to those usually involved in semiconductors) are required to create a band from overlapping donor wave functions and to drive the system metallic around $LaH_{2.8}$. The steady increase of charge carrier density with increasing vacancy density (i.e. decreasing x) is confirmed by Hall effect measurements.

The attractiveness of the strong-correlation picture is that it is local and therefore inherently robust. It is marginally affected by disorder or the overall crystal structure. It also provides a direct explanation for the effective negative charge of H observed in electromigration experiments [3] and the puzzling result of van der Molen *et al.* [7] that, at high temperatures, when H diffuses rapidly, the flux of H atoms measured in $YH_{3-\delta}$ by means of electromigration is equal to the current of electrons. It looks as if during a diffusion jump of a proton, one of the electrons in the original singlet is momentarily lent to the conduction band to be recaptured somewhat later at a neighboring site to reform a singlet.

Second generation switchable mirrors

A major step towards applications was set in 1997 when Van der Sluis *et al.* [8] reported that $Gd_{1-y}Mg_yH_x$ alloys with $y > 0.4$ could be made transparent and colorless in contrast to the yellowish YH_3 (see Fig.1). Moreover, the contrast between the reflecting and the transparent states is enhanced due to the absence of the weak transparency maximum, which is characteristic for YH_2, LaH_2 or REH_2 in their metallic state. In addition $Gd_{1-y}Mg_yH_x$ mirrors switched fast: as shown in Fig.4, the transition from the metallic state to the transparent insulating state occurs in less than 40 ms. The optical gap of $Gd_{0.5}Mg_{0.5}H_{2.5}$ being 3.4 eV, this switchable mirror is color neutral. This color neutrality has also been observed in Y-Mg and La-Mg alloys and is probably a general property of Mg-rare earth alloys. The possibility to fine-tune the optical gap is most important for applications of switchable mirrors.

From a fundamental point of view these Mg-containing alloys confronted us with a new switching process. During the first hydrogen absorption $Y_{0.5}Mg_{0.5}H_x$ disproportionates first into YH_2 and Mg and subsequently, after formation of MgH_2, into a transparent composite of MgH_2 and YH_3. This composite switches back to a metallic composite of YH_2 and Mg . In this transformation Mg acts as a sort of *microscopic shutter* since it switches reversibly from an excellent metal to a large gap (about 6 eV) insulator. This suggested that multilayers of Y (or any rare-earth) and Mg would also act as color neutral switchable mirror which was indeed confirmed experimentally. This is at first sight not extremely surprising since MgH_2 has a much larger optical gap

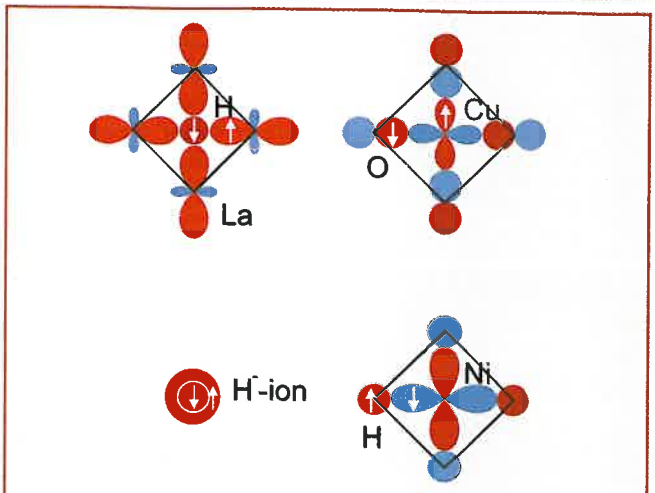


Fig. 3: Correlated singlet states depicted in a plane as antisymmetrized products of atomic-like orbitals. Lobes of opposite sign are shown in red and blue. In $LaH_{2+\delta}$ the singlet involves two electrons and resembles locally a huge H^--ion. In a cuprate such as La_2CuO_4 and the hydride Mg_2NiH_4 it involves two holes at the top of the metal-derived d-band.

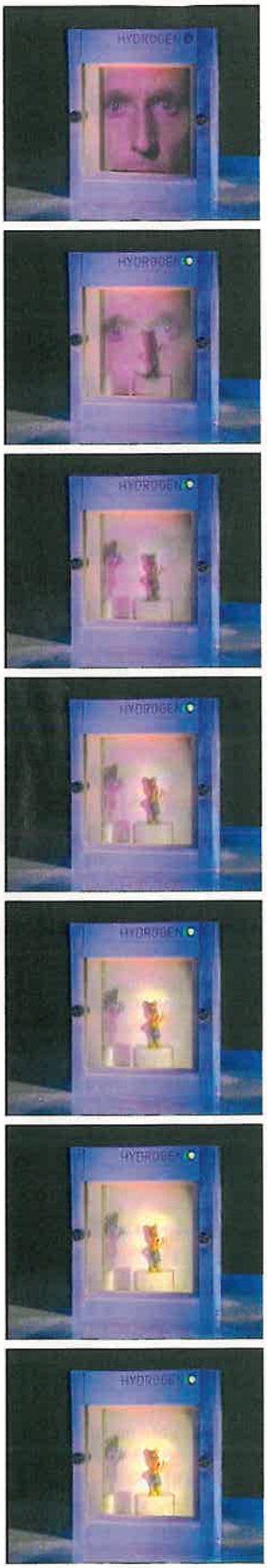
(approx. 6 eV) than YH_3. What is not trivial at all, however, is that the electrical resistivity of $Y_{0.75}Mg_{0.25}H_{2.75}$ is *four* orders of magnitude larger than that of $YH_{3-\delta}$! This cannot be understood in terms of a simple disproportionation and indicates that electronic effects are occurring at the Y-Mg interface.

Third generation switchable mirrors

A few months ago at a conference on electrochromics in Uppsala, Richardson *et al.* (Lawrence Berkeley Labs.) reported that a thin film of a Mg-Ni alloy also exhibited optical switching. This is a major extension of the class of switchable mirrors since it avoids Y, La or rare-earth metals. It is also of fundamental importance since the transparent phase is probably Mg_2NiH_4, a compound in which H and Ni orbitals hybridize strongly to form covalently bonded $(NiH_4)^{4-}$-complexes that are bound ionically to Mg^{2+}-ions. The gap is essentially determined by the most antibonding Ni-H state at the top of the d-band of nickel (see Fig. 3), a situation similar to that in cuprates (for example in La_2CuO_4). Since Mg_2CoH_5 and Mg_2FeH_6 can also be formed, it is probable that new switchable mirror materials based on such compounds will be discovered. This opens a completely new field of investigation of materials with remarkable optical properties in the visible part of the spectrum.

Epitaxial switchable mirrors

So far we have described electrical and optical properties of *polycrystalline* switchable mirrors. We found that it was also possible to synthesize YH_x *epitaxial* films on a transparent and electrically insulating substrate with evaporation at high temperature on a (111)-CaF_2 substrate. The crystallinity of these films deduced from X-ray diffraction is excellent and remains so even after repeated hydrogen loading and unloading. This is in itself remarkable since there is a 15% volume expansion between Y and YH_3! The process through which an epitaxial film can accommodate such high strains without deterioration of its crystallinity was recently identified by Kerssemakers *et al.* [9]. Using *in situ* Atomic Force Microscopy, combined with electrical resistivity and local optical transmission measurements, they discovered that micron-sized triangular domains switch one-by-one, homo-



geneously and essentially independently, during hydrogen absorption. These optically resolvable domains are defined by an extended self-organized ridge network, created during the initial hydrogen loading. The ridges block lateral hydrogen diffusion and act as a microscopic lubricant for the sequentially expanding and contracting domains. This block-wise switching results in a 'Manhattan skyline' in which optical and structural texture are intimately correlated. Their tunability is of technological relevance since it opens the way to a pixel-by-pixel switchable pattern with a minimal amount of inactive surface area. The domain switching of epitaxial films is *locally* very different from the behavior of polycrystalline films, which are optically homogeneous on a micrometer length scale. However, on a macroscopic scale, both polycrystalline and epitaxial switchable mirrors exhibit the same properties.

Conclusions

The great richness of new phenomena in the electrical, optical and mechanical properties of switchable mirror materials, the possibility to fine-tune their properties by alloying and the ease to change continuously their hydrogen content makes them especially attractive for fundamental condensed matter physics. Detailed studies of continuous metal-insulator transitions, fast diffusion and electromigration are drastically simplified since i) the concentration of the dopant (hydrogen) can be modified at willby simply changing the surrounding gas pressure or the voltage in an electrolytic cell, and ii) hydrogen migration can easily be monitored visually. Replacement of hydrogen by deuterium also offers unique opportunities to investigate isotope effects in many physical properties.

Fig. 4: Frames of a video taken during hydrogen absorption by a GdMg switchable mirror. The indicator lights up when gaseous H_2 is introduced in the system. The mirror image of the experimenter fades out rapidly while the little toy bear behind the mirror appears. The time between the first and last frame is 280 ms. The characteristic switching time is approximately 40 ms. (Courtesy P. Duine, Philips Research Labs., Eindhoven).

They offer also interesting possibilities for technological applications, such as smart windows to regulate the light and heat transfer in buildings, antireflection coatings for TV screens and monitors, variable reflectance rear-view mirrors in cars, variable transmittance glasses and smart light bulbs with adaptive optics. Epitaxial switchable mirrors may offer additional possibilities through their self-organized, pixel-by-pixel switchable domain pattern. Recently, two groups at Lawrence Berkeley and at Philips Research Labs [10] have demonstrated the feasibility of all-solid-state devices based on metal-hydride switchable mirrors. In such devices, the mirror layer is separated from a conducting transparent layer of indium-tin oxide by a solid electrolyte (e.g. ZrO_2). Applying a voltage one can control the hydrogen concentration in the switchable mirror and induce reversible switching. Although many materials problems still remain to be solved, such all-solid-state devices are an important step towards large-scale application of switchable mirrors.

Acknowledgements

The author is most grateful to all members (the coauthors in the references and I. A. M. E. Giebels, A. F. T. Hoekstra, J. Isidorsson, A. Remhof, and M. Huisman) of the Condensed Matter Physics group at the Vrije Universiteit for their valuable contributions, to the members of the Switchable Mirror group at Philips Research and of the TMR Research Network 'Metal-hydride films with switchable physical properties' for a fruitful collaboration, and to R. Eder, G. Sawatzky, P. Kelly, P. van Gelderen, T. M. Rice, F. C. Zhang for enlightening discussions. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) and Philips Research. Financial support by the European TMR Programme and the Dutch Ministry of Economic Affairs is also gratefully acknowledged.

References

[1] J.N. Huiberts, R. Griessen, J.H. Rector, R.J. Wijngaarden, J.P. Dekker, D.G. de Groot, and N.J. Koeman, Nature (London) **380**, 231 (1996)

[2] P. Vajda: "Hydrogen in Rare-Earth Metals including RH_{2+x} phases" in *Handbook on the Physics and Chemistry of Rare Earths* **20**, 207 (Elsevier Science 1995) and references therein.

[3] F.J.A. den Broeder, S.J. van der Molen, M. Kremers, J.N. Huiberts, D.G. Nagengast, A.T.M. van Gogh, W.H. Huisman, J.P. Dekker, N.J. Koeman, B. Dam, J.H. Rector, S. Plota, M. Haaksma, R.M.N. Hanzen, R.M. Jungblut, P.A. Duine, and R. Griessen, Nature (London) **394**, 656 (1998)

[4] A.T.M. van Gogh, D.G. Nagengast, E.S. Kooij, N.J. Koeman, and R. Griessen Phys. Rev. Lett. **85**, 2156 (2000)

[5] P. van Gelderen, P. A. Bobbert, P. J. Kelly, G. Brocks, Phys. Rev. Lett. **85**, 2989 (2000) and references therein.

[6] R. Eder, H.F. Pen, and G.A. Sawatzky, Phys. Rev. B **56**, 10115 (1997);K.K. Ng, F.C. Zhang, V.I. Anisimov, and T.M. Rice, Phys. Rev. Lett. **78**, 1311 (1997) and Phys. Rev. B. **59**, 5398 (1999)

[7] S. J. van der Molen, M. S. Welling and R. Griessen, Phys. Rev. Lett. **85**, 3882 (2000)

[8] P. van der Sluis, M. Ouwerkerk, and P.A. Duine, App l. Phys. Lett. **70**, 3356 (1997)

[9] J. W. J. Kerssemakers, S. J. van der Molen, N. J. Koeman, R. Günther and R. Griessen, Nature **396**, 489 (2000)

[10] R. Griessen and P. van der Sluis, Schaltbare Spiegel, Physik in unserer Zeit (2), (2001) and references therein.